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Synthesis and characterization of alternating poly(amide urea)s and poly(amide urethane urethane)s from ε-caprolactam, diamines, and diphenyl carbonate or ethylene carbonate

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Abstract: Alternating poly(amide urea)s from ε-caprolactam, diamines H_2N-$(CH_2)_x$-NH_2 (x = 2 - 4), and diphenyl carbonate were prepared in two steps. The microstructure of the poly(amide urea)s, as determined by means of ^{1}H NMR spectroscopy, reveals a strictly alternating sequence of the building blocks. The molecular weights and polydispersities obtained were 7500 < M_n < 10 000 and 1.48 < M_w/M_n < 1.56, respectively. Thermal properties were determined by means of differential scanning calorimetry (DSC) (163.9°C < T_m < 197.2°C; 55.5°C < T_g (2nd heating) < 72.2°C), and thermogravimetric analysis (TGA). TGA shows a three-step decomposition at 200, 350, and 450°C, which was attributed to the cleavage of *O*-phenyl urethane end groups, as well as urea and amide linkages. These assignments were made by comparison with model compounds. Furthermore, alternating poly(amide urethane urethane)s from ε-caprolactam, diamines, and ethylene carbonate were prepared in three steps. The microstructure of the poly(amide urethane urethane)s, as determined by means of ^{1}H NMR spectroscopy, reveals imperfections. The molecular weights and polydispersities obtained were 5400 < M_n < 17 000 and 2.08 < M_w/M_n < 2.99, respectively. Thermal properties were determined by means of DSC (155.9°C < T_m < 159.0°C; 35.5°C < T_g (2nd heating) < 39.0°C) and TGA. TGA shows a complex decomposition due to the formation of ethylene carbonate by cleavage of the urethane groups (at approx. 230°C) and formation of poly(amide urea)s. The newly formed poly(amide urea)s decompose in a similar way as the poly(amide urea)s.

Introduction

Three important classes of polymers with carbon, oxygen, and nitrogen atoms in the main chain are polyamides, polyurethanes, and polyureas. Linear [*m*,*n*]-polyamides are prepared via polycondensation of an AA with a BB monomer, e.g., a diamine and a dicarboxylic acid. AB monomers, e.g., lactams, are used for the preparation of [*n*]-polyamides [1]. Commercially manufactured polyurethanes are prepared from di- or polyfunctional hydroxy compounds and di- or polyfunctional isocyanates. Polyurethanes but also urethane-containing copolymers are widely used to make foams,

fibres, elastomers, adhesives, and coatings [2–4]. The chemistry and technology of polyureas began in the 1960s, which is relatively late compared to polyamides and polyurethanes. Nowadays, polyureas are prepared from aliphatic, aromatic or heterocyclic polyamines (mainly diamines) with carbon dioxide, carbon oxysulfide, carbonic acid esters, phosgene, urea, urethanes, or isocyanates [5].

In order to cover a wide range of properties, it is interesting to prepare polymers with different functional groups. The properties of these polymers are not only determined by the building blocks but also by the concentration and by the distribution – random or regular – of the functional groups. Excellent examples of this principle are the poly(ester amide)s [6-17]. Due to hydrogen bonds between the amide groups, these materials have improved mechanical and thermal properties compared with polyesters; the ester groups are mainly responsible for hydrolytical degradation.

The aim of this work is to synthesize alternating poly(amide urea)s and alternating poly(amide urethane urethane)s by using ε-caprolactam, diamines, and diphenyl carbonate or ethylene carbonate. These polymers contain amide and urea or urethane groups thus combining the properties of three important classes of polymers with carbon, oxygen, and nitrogen in the main chain.

Experimental part

Materials

ε-Caprolactam (BASF), 1,2-diaminoethane (BASF), 1,3-diaminopropane (BASF), 1,4-diaminobutane (67.5 wt.-% in water, DSM), diphenyl carbonate (Merck), ethylene carbonate (Acros Organics), and dibutyldimethoxytin ($Bu_2Sn(OMe)_2$, Aldrich) were used as received.

Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 and 75 MHz, respectively. Chloroform ($CDCl_3$), dimethyl sulfoxide (DMSO-d_6), formic acid (DCOOD), and trifluoroacetic acid (TFA-d_1) were used as solvents, and tetramethylsilane (TMS) served as internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high-pressure liquid chromatography pump (Bischoff HPLC pump 2200) and a refractive index detector (Waters 410). The eluting solvent was *N*,*N*-dimethylacetamide (DMAc) with 2.441 g/L LiCl.

The flow rate was 0.8 mL/min. Four columns with MZ-DVB gel were applied: length of each column 300 mm, diameter 8 mm, diameter of gel particles 5 µm, nominal pore width 100 Å, 100 Å, 10^3 Å, 10^4 Å. Calibration was achieved using polystyrene standards of narrow molecular weight distribution from Polymer Standard Service, Mainz.

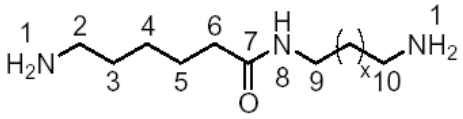
Differential scanning calorimetric (DSC) analyses were performed with a Netzsch DSC 204 in nitrogen atmosphere with a heating rate of 10 K/min. Calibration was achieved using indium standard samples.

Thermogravimetric analyses (TGA) were performed on a TG 209 with a TA-System-Controller TASC 414/2 from Netzsch. The measurements were performed in nitrogen atmosphere with a heating rate of 10 K/min.

Syntheses

Amide-diamines **3a**-**c**

6-Aminohexanoic acid 3-aminopropylamide **3b**: ε-Caprolactam (9.09 g, 80.3 mmol), 1,3-diaminopropane (33.8 mL, 402 mmol), and water (13 mL) were heated in an autoclave at 200°C for 20 h while the pressure increased to 4.6 bar. After cooling, excess of 1,3-diaminopropane and water was removed in vacuum at 35°C and yellow oil was left. All amide-diamines **3a**-**c** were prepared according to the same procedure (Tab. 1).



3

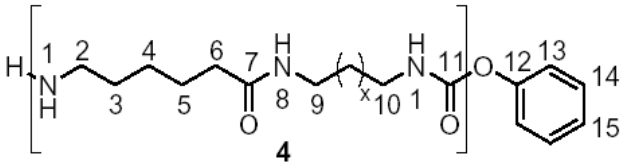
x = $(CH_2)_0$ - $(CH_2)_2$

Tab. 1. Yield and NMR data of amide-diamines **3a**-**c**

ID	Yield	Solvent	Characteristic ^{1}H and ^{13}C NMR data (δ in ppm)					
	%		CH_2-2	CH_2-10	CH_2-6	C-7	CH_2-9	H-8
3a	93	$CDCl_3$	2.68	2.81	2.20	-	3.27	7.07
			41.90	41.50	36.47	173.57	42.16	-
		DMSO-d_6	2.50	2.54	2.05	-	3.01	7.80
			41.48	41.38	35.42	172.08	42.21	-
3b	92	$CDCl_3$	2.68	2.76	2.18	-	3.31	7.16
			41.94	39.80	36.51	173.30	37.28	-
		DMSO-d_6	2.50	2.51	2.03	-	3.06	7.82
			41.52	39.02	35.46	171.94	35.96	-
3c	80	$CDCl_3$	2.68	2.70	2.17	-	3.22	6.87
			41.85	41.63	36.48	173.17	39.18	-
		DMSO-d_6	2.50	2.51	2.03	-	3.00	7.85
			41.54	41.37	35.51	171.91	38.35	-

Poly(amide urea) **4a**

Amide-diamine **3a** (1.73 g, 10.0 mmol) was added to diphenyl carbonate (2.14 g, 10.0 mmol) in a condensation flask. Polycondensation was performed at 100°C for 1 h at normal pressure and 2 h at reduced pressure (10^{-2} mbar) with removal of phenol by distillation. For purification, the polymer was dissolved in formic acid (10 mL) and precipitated in diethyl ether (100 mL). The product was isolated by filtration and dried in vacuum at 50°C. All poly(amide urea)s **4a**-**c** were prepared according to the same procedure (Tab. 2 and Tab. 3).



4

x = $(CH_2)_0$ - $(CH_2)_2$

Tab. 2. NMR data of the alternating poly(amide urea)s **4a**-**c**

ID	S	Characteristic ^{1}H and ^{13}C NMR data (δ in ppm)							
		CH_2-2	CH_2-9	CH_2-10	CH_2-6	C-7	C-11	H-8	H-1
4a	D	3.05	3.05	3.05	2.07	-	-	7.54	5.72
		40.01	39.73	39.84	35.92	172.70	158.75	-	-
	F	3.22	3.48	3.48	2.40	-	-	10.45	10.45
		35.84	34.85	35.59	30.67	172.80	155.50	-	-
4b	D	3.01	3.01	3.01	2.04	-	-	7.78	5.83
		39.55	36.45	37.28	35.80	172.43	158.72	-	-
	T	3.31	3.45	3.30	2.53	-	-	11.50	11.50
		41.47	38.60	38.96	34.11	181.24	179.87	-	-
4c	F	3.54	3.98	3.54	2.65	-	-	10.52	10.52
		35.57	34.73	35.28	30.57	172.34	155.30	-	-
	T	3.38	3.61	3.38	2.75	-	-	11.71	11.71
		43.79	42.97	43.28	35.53	181.43	161.16	-	-

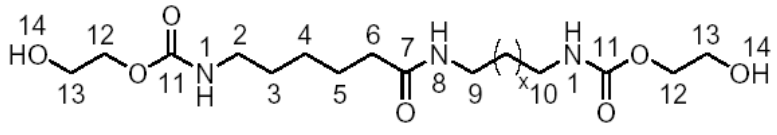
S = solvent, D = DMSO-d_6 at 80°C, T = TFA-d_1, F = DCOOD

Tab. 3. Yield and molecular weight of the alternating poly(amide urea)s **4a**-**c**

Compound	Yield in %	M_n	M_w	M_w/M_n
4a	67	10 000	16 000	1.56
4b	82	7500	11 000	1.48
4c	95	not soluble in DMAc at 80°C		

α,ω-Diols **5a**-**c**

5-[3-(2-Hydroxyethoxycarbonylamino)propylcarbamoyl]pentylcarbamic acid 2-hydroxyethyl ester **5b**: A solution of ethylene carbonate (3.12 g, 35.4 mmol) in ethylene glycol (22 mL) was added slowly to the amide-diamine **3b** (2.17 g, 11.8 mol). After stirring for 23 h at room temperature, ethylene glycol was removed in vacuum (10^{-2} mbar) at 60°C to give a colourless wax (yield: 93%). All α,ω-diols **5a**-**c** were prepared according to the same procedure; yields were between 90% and 100% (Tab. 4).



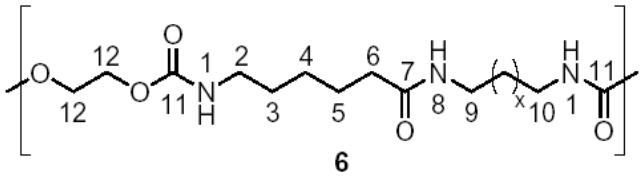
5

x = $(CH_2)_0$ - $(CH_2)_2$

Poly(amide urethane urethane) **6c**

α,ω-Diol **5c** (2.50 g, 6.62 mmol) and dibutyldimethoxytin (97.2 µL, 0.13 g) were heated at 150°C and normal pressure for 1 h while the mixture melted. Subsequently, ethylene glycol was removed in vacuum (10^{-2} mbar) for 4.5 h. For purification, the polymer was dissolved in formic acid (15 mL) and precipitated in diethyl ether (250 mL). The product was isolated by filtration and dried in vacuum at 50°C. Poly(amide urethane urethane) **6b** was prepared according to the same procedure; poly(amide

urethane urethane) **6a** was prepared by heating the α,ω-diol **5a** for 3 h in vacuum (Tab. 5).



6

x = $(CH_2)_0$ - $(CH_2)_2$

Tab. 4. NMR data of the α,ω-diols **5a**-**c**

ID	S	Characteristic ^{1}H and ^{13}C NMR data (δ in ppm)						
		CH_2-2	CH_2-10	CH_2-9	C-11	H-1	CH_2-12	CH_2-13
4a	D	3.05	3.05	3.05	-	7.06/7.09	3.94	3.53
		40.44	40.40	38.85	56.70	-	65.94	59.79
	F	3.21	3.43	3.50	-	9.63	4.48	4.41
		35.69	35.02	34.64	153.28	-	60.47	55.07
	T	3.28	3.57	3.73	-	9.36	4.69	4.62
		43.67	42.60	41.13	160.53	-	70.78	61.82
4b	D	3.00	3.00	3.00	-	7.08	3.94	3.52
		40.47	38.34	36.43	156.69	-	65.86	59.82
	T	3.33	3.42	3.68	-	11.38	4.70	4.54
		42.70	41.68	39.90	160.96	-	67.91/68.84[1]	62.98/65.18[1]
4c	D	2.96	2.96	2.96	-	7.08/7.10	3.93	3.52
		41.58	41.40	38.48	156.70	-	65.77	59.84
	T	3.35	3.35	3.63	-	11.09	4.44	4.44
		44.24	42.65	42.38	160.89	-	67.88/70.55[1]	61.96/63.05[1]

S = solvent, D = DMSO-d_6, T = TFA-d_1, F = DCOOD

[1] TFA-d_1 reacts with the hydroxyl group of the α,ω-diol to form the ester.

Tab. 5. Yield, M_n, M_w/M_n, and NMR data of poly(amide urethane urethane)s **6a**-**c**

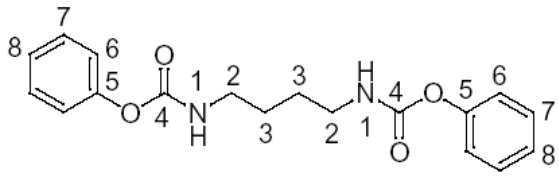
ID	Yield %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	S	Characteristic ^{1}H and ^{13}C NMR data (δ in ppm)				
					CH_2-12	C-11	C-7	H-1	H-8
6a[1]	60	5400	2.10	D	4.08	-	-	7.18	7.80
					62.69	156.31	172.63	-	-
				T	4.48	-	-	11.59	11.59
					66.37	161.32	182.40	-	-
6b	70	12000	2.08	D	4.08	-	-	7.18	7.75
					62.76	156.31	172.43	-	-
				F	4.34	-	-	10.37	10.37
					58.80	153.32	172.42	-	-
6c	80	17000	2.99	D	4.08	-	-	7.18	7.74
					62.70	156.33	172.26	-	-

S = solvent, D = DMSO-d_6, T = TFA-d_1, F = DCOOD

[1] Reaction time 3 h instead of 4.5 h.

4-Phenoxycarbonylaminobutylcarbamic acid phenyl ester (1,4-butanediphenyl-urethane)

1,4-Diaminobutane (2.30 g, 26.1 mmol) was added slowly to a solution of diphenyl carbonate (16.78 g, 78.3 mmol) in methylene chloride (35 mL). After stirring for 10 min, a colourless solid was formed, which was filtered, washed with methylene chloride (10 mL), and dried in vacuum at 50°C. Yield: 7.95 g (24.2 mmol, 93 %).



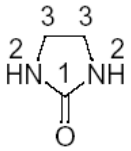
^{1}H NMR (DMSO-d_6): δ = 1.53 (m, 4H, H-3), 3.10 (m, 4H, H-2), 7.06 - 7.12 (m, 4H, H-6), 7.14 - 7.21 (m, 2H, H-8), 7.30 - 7.40 (m, 4H, H-7), 7.78 (t, 2H, H-1, ^{3}J = 5.3 Hz).

^{13}C NMR (DMSO-d_6): δ = 26.99 (C-3), 40.55 (C-2), 122.13 (C-6), 125.20 (C-8), 129.74 (C-7), 151.51 (C-5), 154.78 (C-4).

Thermal decomposition of the poly(amide urea)s **4a** and **4b**

The poly(amide urea) **4a** (0.94 g) was heated in vacuum (10^{-2} mbar) for 12 h at 205°C and colourless crystals were collected in a cold trap. The product contained dimethylene urea **7** and ε-caprolactam with a mole ratio of 6.7 : 1. Yield: 0.15 g (1.69 mmol), product mixture of dimethylene urea (0.13 g, 1.47 mmol, 31 mol-%) and ε-caprolactam (0.025 g).

Dimethylene urea **7**

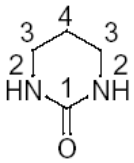


^{1}H NMR (TFA-d_1): δ = 3.87 (m, 4H, H-3), 11.46 (s, H-2).

^{13}C NMR (TFA-d_1): δ = 43.45 (C-3), 167.36 (C-1).

Poly(amide urea) **4b** (1.01 g) was heated in vacuum (10^{-2} mbar) for 6 h at 205°C and trimethylene urea **8** was collected in a cold trap. Yield: 0.16 g (1.57 mmol, 33 mol-%).

Trimethylene urea **8**



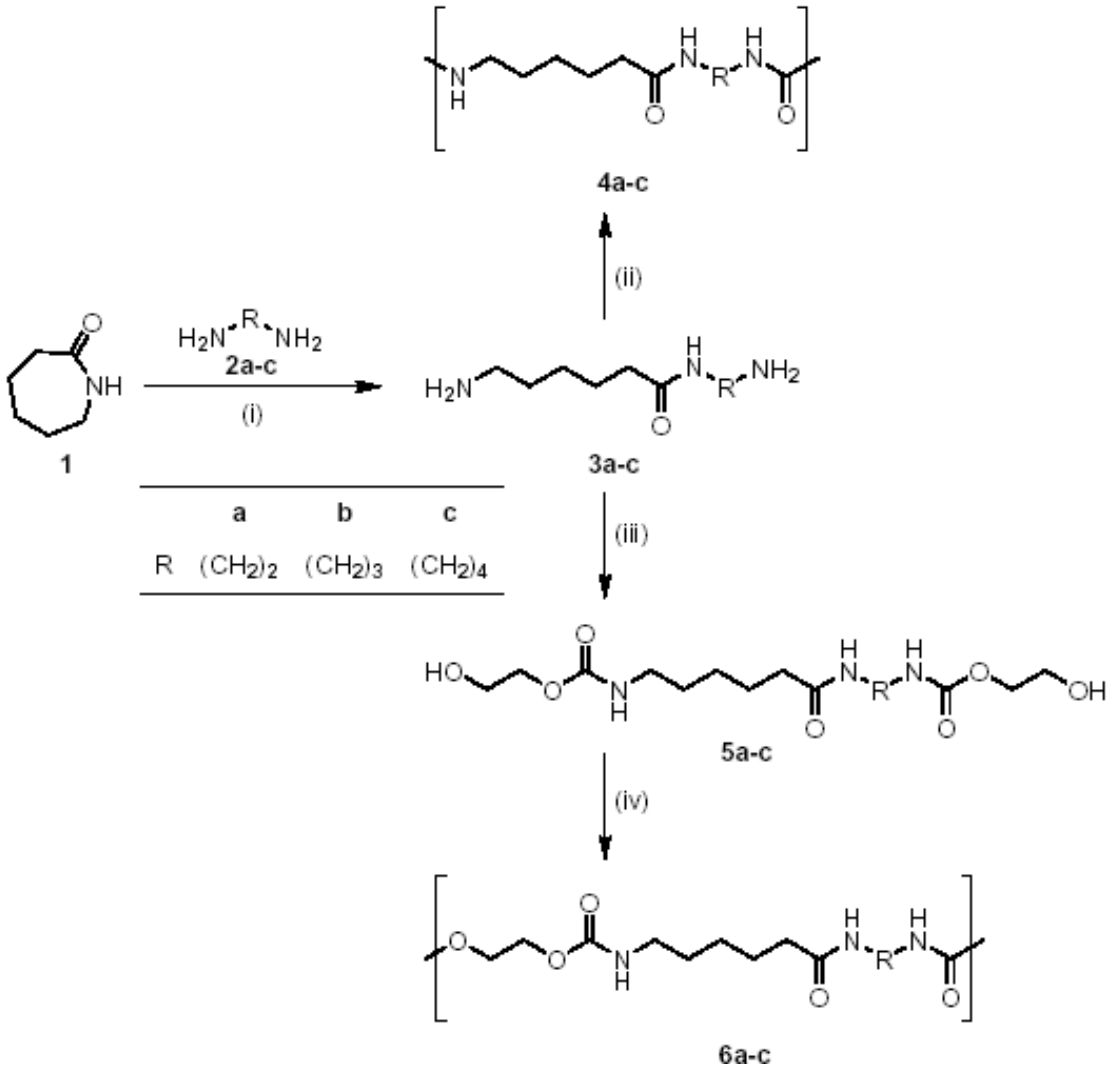
^{1}H NMR (TFA-d_1): δ = 2.10 (m, 2H, H-4), 3.55 (m, 4H, H-3), 11.95 (s, H-2).

^{13}C NMR (TFA-d_1): δ = 20.34 (C-4), 40.97 (C-3), 159.57 (C-1).

Results and discussion

There are only a few scientific papers dealing with alternating poly(amide urea)s and/or poly(amide urethane)s. Mormann et al. reported the synthesis of regular poly(amide urethane)s by using diamido-diisocyanates and butane-1,4-diol as starting materials [18]. In our group alternating poly(amide urethane)s were prepared from ε-caprolactam, amino alcohols, and diphenyl carbonate or ethylene carbonate; the results will be published soon [19,20].

Alternating poly(amide urea)s were obtained from ε-caprolactam **1**, a homologous series of diamines **2a**-**c**, and diphenyl carbonate in two steps. Alternating poly(amide urethane urethane)s were obtained from ε-caprolactam **1**, a homologous series of diamines **2a**-**c**, and ethylene carbonate in three steps. In both cases, the diamines react first with ε-caprolactam via ring opening to form the amide-diamines **3a**-**c**. These subsequently react with diphenyl carbonate in bulk to give the poly(amide urea)s **4a**-**c**. The amide-diamines **3a**-**c** were reacted with ethylene carbonate to give the corresponding α,ω-diols **5a**-**c**, which finally were converted to the corresponding poly(amide urethane urethane)s **6a**-**c** by polycondensation in bulk (Scheme 1).



Scheme 1. Synthesis of alternating poly(amide urea)s and alternating poly(amide urethane urethane)s from ε-caprolactam, diamines, and diphenyl carbonate or ethylene carbonate. (i) ε-caprolactam/**2a**-**c** = 1/5, H_2O, *T* = 200°C in an autoclave, *t* = 24 h; (ii) diphenyl carbonate/**3a**-**c** = 1/1, *T* = 100°C, *t* = 1 h at normal pressure, *t* = 2 h

at reduced pressure (10^{-2} mbar); (iii) ethylene carbonate in ethylene glycol (1.6 M)/ **3a**-**c** = 3/1, room temp., *t* = 24 h; (iv) **5a**-**c**, 5 wt.-% $Bu_2Sn(OMe)_2$, *T* = 150°C, *t* = 1 h at normal pressure, *t* = 3 - 5 h at reduced pressure (10^{-2} mbar)

The amide-diamines **3a**-**c** were obtained by aminolysis of ε-caprolactam with excess of diamine to circumvent the formation of higher oligomers. A temperature of 200°C and the presence of water are necessary to induce the ring opening of ε-caprolactam. For the preparation of the poly(amide urea)s **4a**-**c**, the amide-diamines **3a**-**c** were treated with diphenyl carbonate in bulk at 100°C. ^{1}H and ^{13}C NMR spectra of the purified products **4a**-**c** show that the obtained poly(amide urea)s have a regular microstructure comprising alternating amide and urea linkages. However, the asymmetrically substituted urea groups are expected to be randomly distributed (Bernoulli statistics). ^{1}H and ^{13}C NMR spectra of the poly(amide urea)s in DMSO-d_6 clearly show distinct resonance signals for each methylene group and two distinct resonance signals for the urea and amide groups with an intensity ratio of 2 : 1 at 5.72 (158.75) and 7.53 (172.70) ppm, respectively (Fig. 1). The characteristic chemical shifts of the methylene groups adjacent to the amide and urea groups are given in the Exptl. part.

The absolute molecular weights of the poly(amide urea)s obtained were determined by means of end group analysis and were calculated to be 550 < M_n < 1750. Therefore, the CH_2 proton of the ε-caprolactam moiety adjacent to the amide group was compared with the protons of the *O*-phenyl end group. Hence, oligomers up to the octamer are formed.

Furthermore, the number-average molecular weights and polydispersities were determined by means of GPC and were found to be 7500 < M_n < 10000 and 1.48 < M_w/M_n < 1.56, respectively. The relatively low polydispersities are explained by the fact that low molecular weight material is soluble in diethyl ether. The yields of the poly(amide urea)s **4a**-**c** were between 67% and 95% (Tab. 3).

For the preparation of the poly(amide urethane urethane)s **6a**-**c**, an attempt was made to prepare the α,ω-diols from the amide-diamines **3a**-**c** and ethylene carbonate in water at room temperature. The ^{1}H NMR spectrum, however, shows the formation of ethylene glycol. Furthermore, the ratio of integrals of the proton resonance lines of the methylene groups HO-CH_2CH_2-OCONH- to those of -CH_2CONH- was not 2 : 1 but 1.2 : 1. To reduce the possibility of transesterification reactions, the reaction was carried out in ethylene glycol. A nucleophilic attack of the hydroxyl group of ethylene glycol at the carbonyl carbon atom of an α,ω-diol leads in a degenerated reaction to the reactant. Hence, the amide-diamines **3a**-**c** were treated with ethylene carbonate in ethylene glycol at room temperature to give the corresponding α,ω-diols **5a**-**c** in good yields.

The amount of carbonic acid ester, in this case ethylene carbonate, plays a key-role in the formation of the desired product or the by-product. For the preparation of the α,ω-diols **5a**-**c** excess of ethylene carbonate (more than 2 mol of ethylene carbonate per 1 mol of diamine) was used to circumvent the formation of urea linkages by a nucleophilic reaction of the amine of the amide-diamine at the carbon atom of the urethane group of the α,ω-diol. However, this side-reaction could not be avoided in aqueous solution. For the preparation of the poly(amide urea)s **4a**-**c** urea linkages are aimed and therefore 1 mol of carbonic acid ester, i.e., diphenyl carbonate, is reacted with 1 mol of amide-diamines **3a**-**c**.

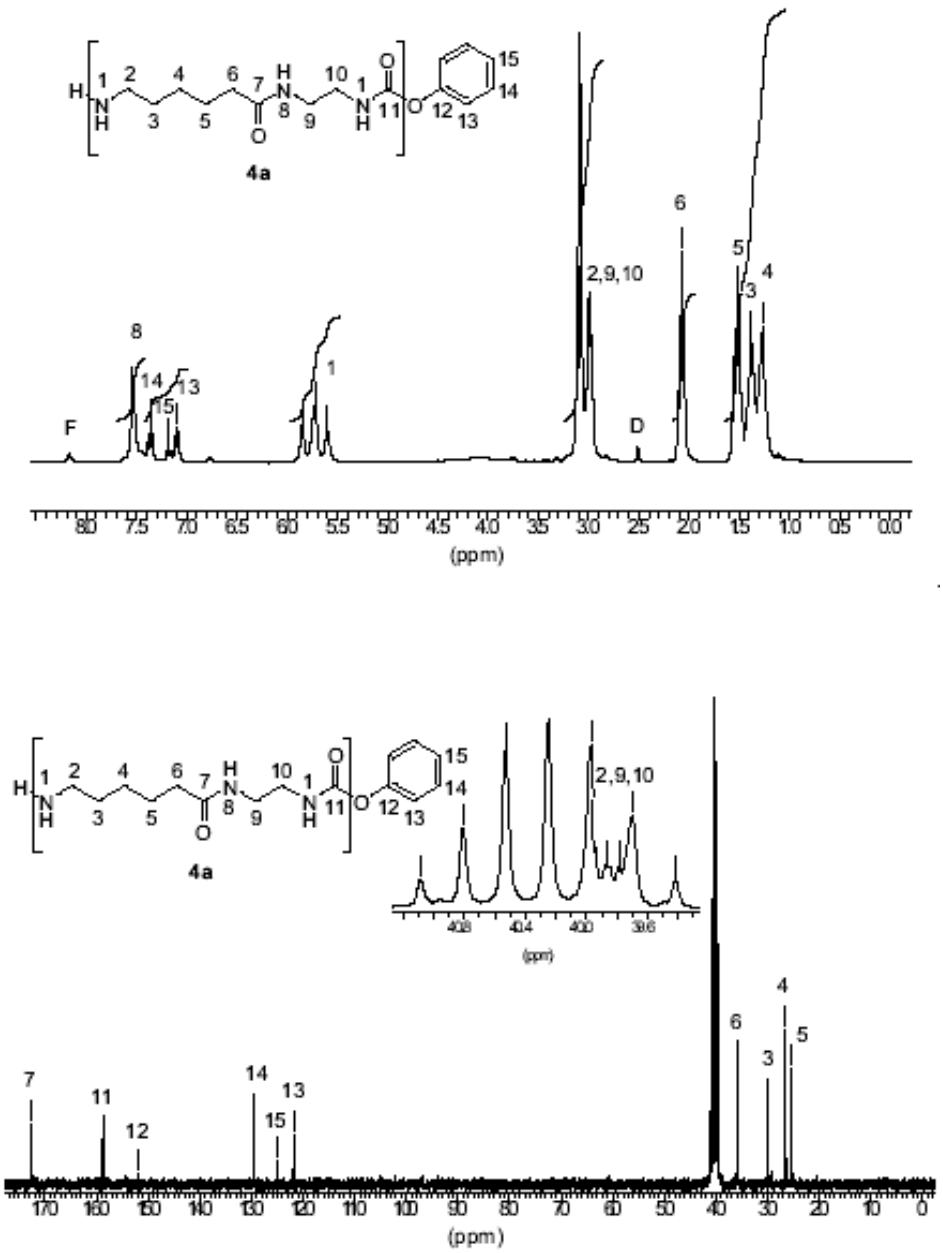


Fig. 1. ^{1}H and ^{13}C NMR spectra of poly(amide urea) **4a** in DMSO-d_6 (D = DMSO; F = formic acid)

The α,ω-diols **5a**-**c** were used as starting material for the polycondensation performed in bulk in the presence of 5 wt.-% $Bu_2Sn(OMe)_2$ as a catalyst. To find the proper reaction temperature, the polycondensation of the α,ω-diol **5a** was carried out at three different temperatures, each for 3 h, after which a sample was taken for GPC analysis. The GPC curve of the α,ω-diol **5a** shows two peaks (Fig. 2), a high peak (product) at V_e = 34 mL and a small peak (dimer) at approximately V_e = 33 mL indicating that the formation of dimers cannot be prevented completely. The GPC curve shows two additional peaks after 3 h of polycondensation in vacuum (10^{-2} mbar) at V_e = 32.5 mL and at V_e = 31.5 mL (shoulder). The intensities of both peaks of the monomer have decreased. After another 3 h of polycondensation at 125°C, the GPC curve shows a similar pattern with different intensity ratio. Moderate molecular weights of M_n = 5400 (M_w/M_n = 2.10) are found after another 3 h in vacuum (10^{-2} mbar) at 150°C.

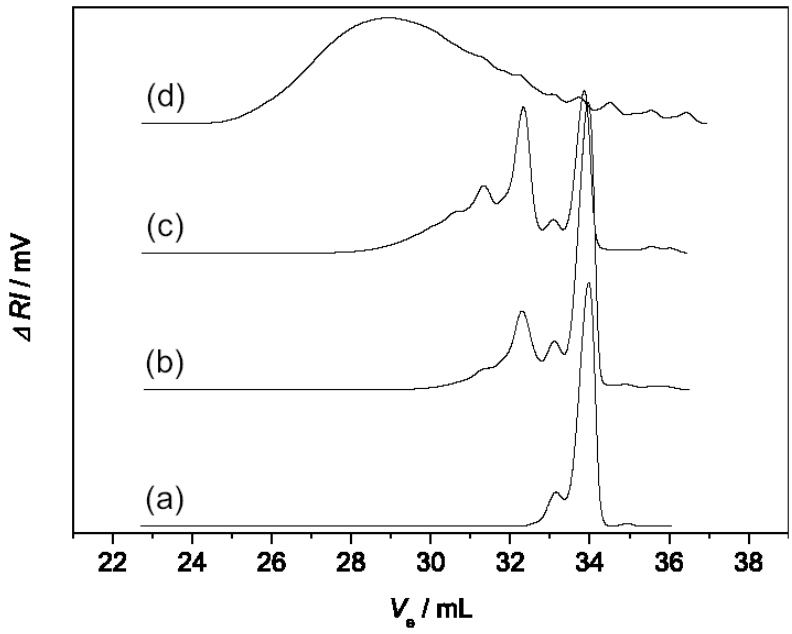


Fig. 2. GPC curves of α,ω-diol **5a** (curve a) and poly(amide urethane urethane) **6a** after 3 h heating in vacuum at T = 100°C (curve b), T = 125°C (curve c), and T = 150°C (curve d)

NMR spectra (in DMSO-d_6) show only the characteristic resonance signals of polymer **6a** at 150°C. Separate resonance signals for the repeating unit and the *O*-hydroxyethylurethane end groups were found at temperatures lower than 150°C.

The α,ω-diols **5b** and **5c** were used as starting material for the polycondensation performed in bulk for 4.5 h at 150°C in the presence of 5 wt.-% $Bu_2Sn(OMe)_2$ as a catalyst. ^{1}H NMR spectra of the purified products **6a**-**c** show two distinct resonance signals for the proton of the amide and urethane groups with an intensity ratio of 1 : 2 at 7.74 and 7.18 ppm, respectively. Two resonance signals are found for the urethane protons, which are attributed to the *E* and *Z* conformers. The characteristic chemical shifts of the methylene groups adjacent to the amide and urethane groups are given in the Exptl. part. The ^{1}H NMR spectrum (δ = 5.76 ppm) as well as the ^{13}C NMR spectrum (δ = 162.36 ppm), with **6c** as an example, shows an additional signal, which is attributed to a urea group. This means that the obtained poly(amide urethane urethane)s exert defects in their microstructure (Fig. 3).

The obtained poly(amide urethane urethane)s **6a**-**c** show bimodal elution curves in GPC (2.08 < M_w/M_n < 2.99). They precipitate in the reaction vessel after a certain conversion has been reached leading to a heterogeneous system (Tab. 5).

Thermal properties

Thermogravimetric analyses of the poly(amide urea)s **4a**-**c** show that they decompose in three steps to form volatile products (Fig. 4). It was assumed that the first maximum (at approximately 200°C) corresponds to the cleavage of the *O*-phenylurethane end group and the second maximum (at approx. 350°C) to the cleavage of the urea groups. The third maximum (at approx. 450°C) seems to show the same decomposition characteristics as polyamides. Here it should be mentioned that the relatively high intensity of the first decomposition maximum is due to the low molecular weights of the poly(amide urea)s analyzed.

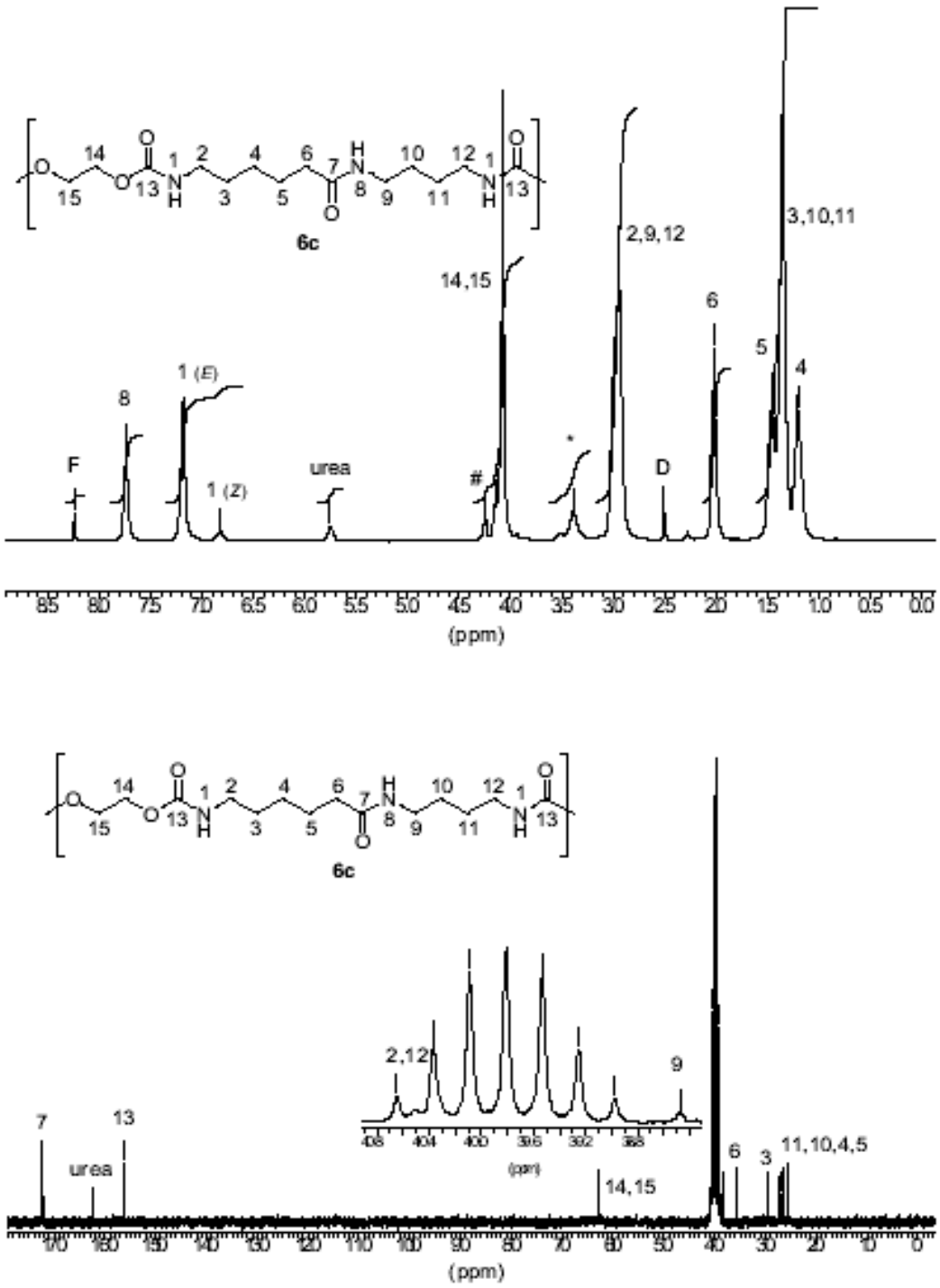


Fig. 3. ^{1}H and ^{13}C NMR spectra of poly(amide urethane urethane) **6c** in DMSO-d_6 (D = DMSO; F = formic acid; * = water; # = end group)

To confirm these assignments, TGA of polyamide-6 and 1,4-butane diphenylurethane was performed. Both compounds show decomposition in one step to form volatile products. Polyamide-6 decomposes with a maximum at approx. 450°C. The pyrolytic decomposition of polyamides in an inert medium is of radical character. The probability of splitting is the highest for the bonds in β-position to carbonyl, scission of the amide bond according to the Norrish reaction I comes next [21]. 1,4-Butane diphenylurethane decomposes with a maximum at approx. 240°C. To investigate the volatile products formed during decomposition, the poly(amide urea)s **4a**-**c** were heated in

vacuum (10^{-2} mbar for 6 h to 12 h at 205°C) and the volatile products were condensed in a cold trap (Scheme 2).

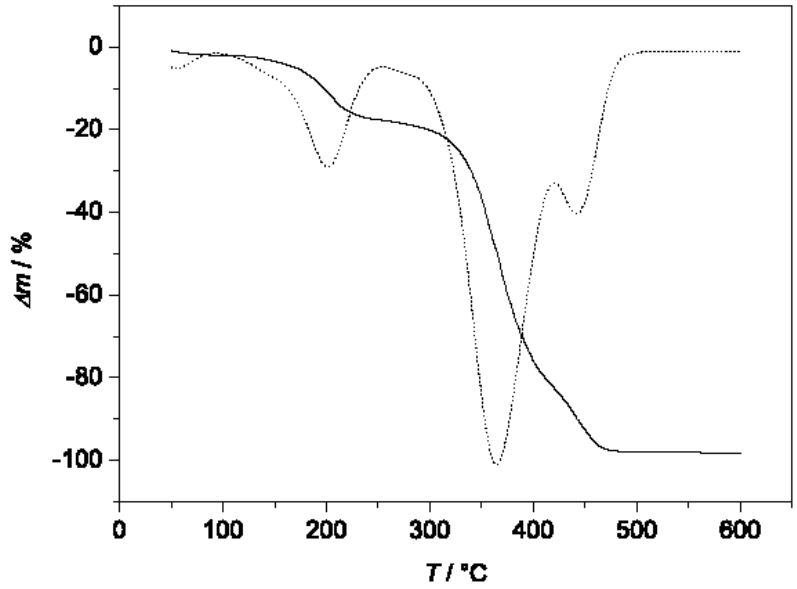
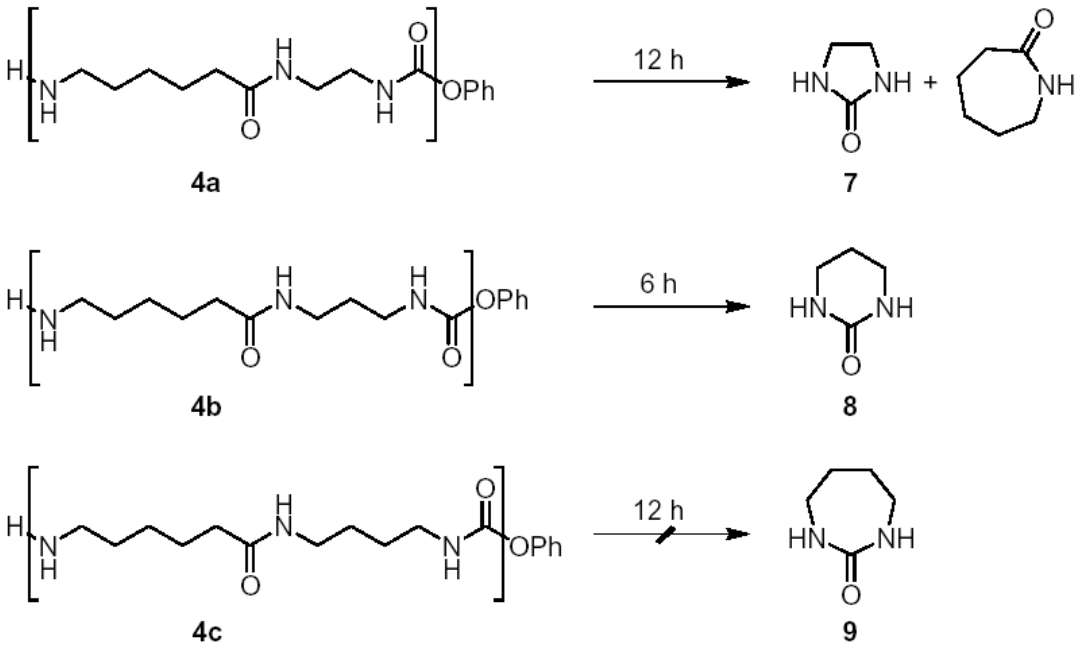


Fig. 4. TGA of poly(amide urea) **4c**; (· · ·) differential curve

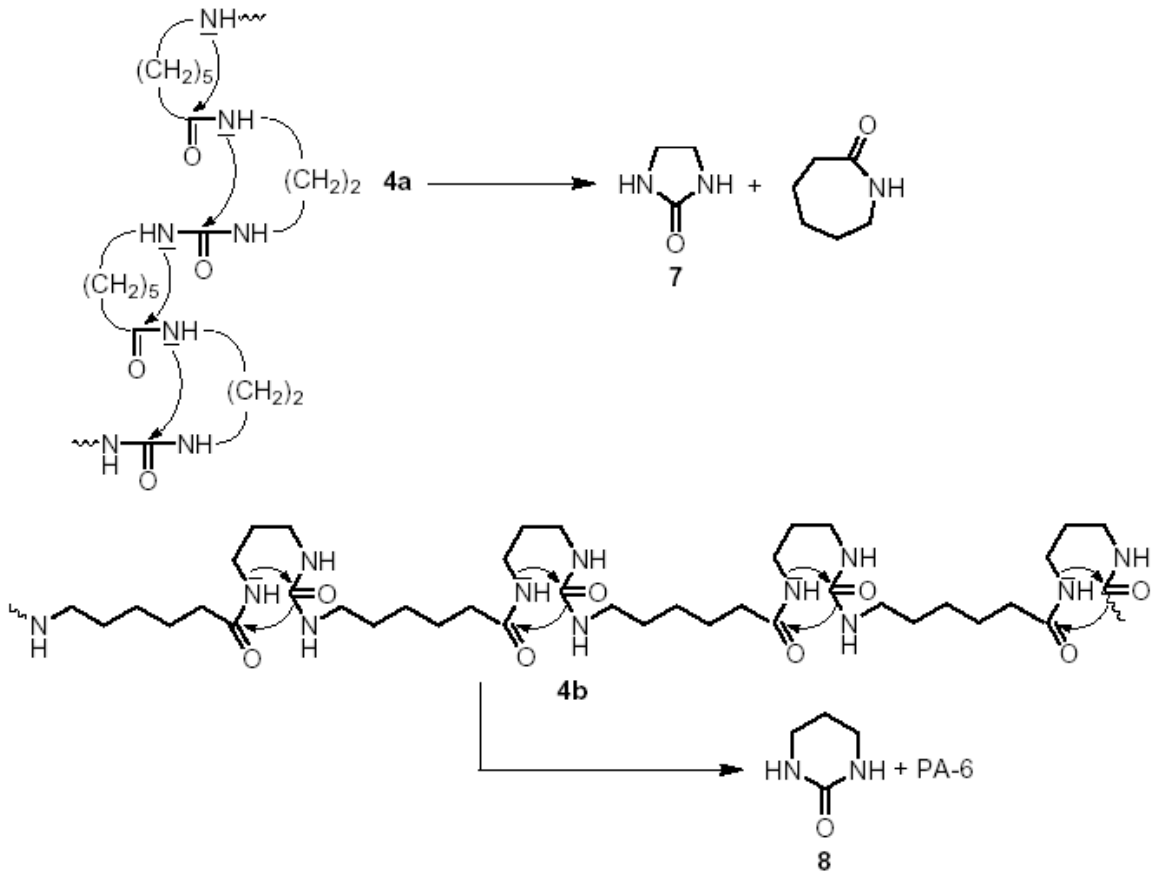


Scheme 2. Thermal decomposition of poly(amide urea)s **4a**-**c** and formation of cyclic ureas (T = 205°C, t = 12 h for **4a** and **4c** and t = 6 h for **4b**, 10^{-2} mbar)

Under these conditions, volatile products were obtained from poly(amide urea)s **4a** and **4b**, however, not from **4c**. NMR spectroscopic investigations of the volatile products reveal that from **4a** ε-caprolactam and dimethylene urea **7** (yield: 31 mol-%) and from **4b** only trimethylene urea **8** (yield: 33 mol-%) is formed. Presumably two different mechanisms are operating. The decomposition of the poly(amide urea) **4a** leads to dimethylene urea **7** and at the same time to ε-caprolactam. Upon decom-

position of poly(amide urea) **4b** only trimethylene urea **8** is formed and it is assumed that PA-6 is left. Scheme 3 shows how for conformational reasons the formation of these products can be explained. Calculations have to be used to confirm or to refute these assumptions. All residues are insoluble in TFA-d_1; they only swell. Thus cross-linked products are expected to be formed by reaction of urea and amide NH groups with isocyanates. The formation of isocyanates, albeit only in small concentrations, is likely at these high temperatures.

Thermogravimetric analyses of the poly(amide urethane urethane)s **6a**-**c** are more complex due to the formation of ethylene carbonate by cleavage of the urethane groups (at *c*. 230°C) and formation of poly(amide urea)s (Fig. 5). The newly formed poly(amide urea)s decompose in a similar way as poly(amide urea)s **4a**-**c** (Tab. 6).



Scheme 3. Postulated mechanism for the decomposition of the poly(amide urea)s **4a** and **4b**

Tab. 6. Decomposition temperatures of the obtained poly(amide urea)s **4a**-**c** and poly(amide urethane urethane)s **6a**-**c** determined by means of TGA

Sample	*T* °C	*T* °C	*T* °C	*T* °C	*T* °C	*T* °C	*T* °C
4a		185				343	457
4b		217				347	443
4c		201				363	458
6a			229		306		445
6b	168		229	288	315		439
6c			238	265	320	342	442

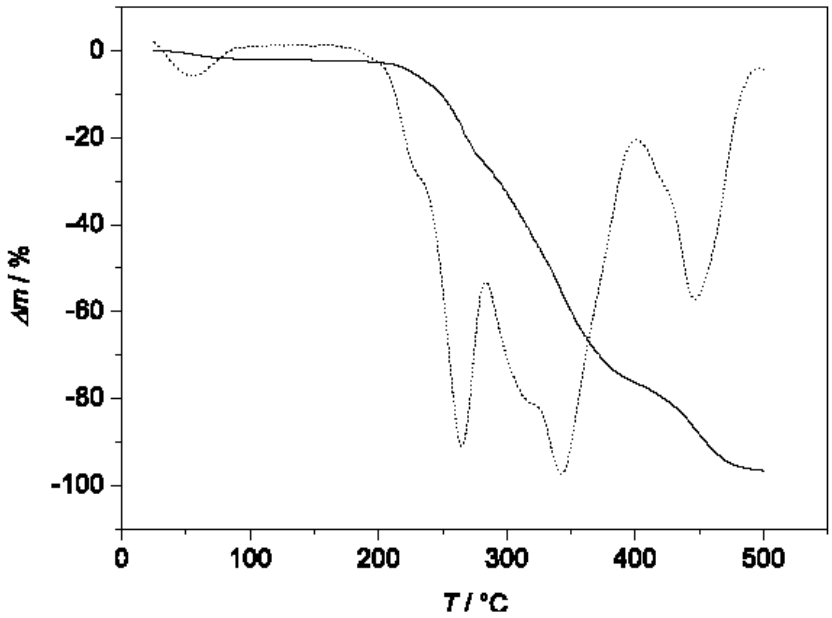


Fig. 5. TGA of poly(amide urethane urethane) **6c**; (· · ·) differential curve

Thermal properties of poly(amide urea)s **4a**-**c** and poly(amide urethane urethane)s **6a**-**c** were determined by means of DSC (Tab. 7). Poly(amide urea)s **4a** and **4b** are semi-crystalline polymers showing a T_g and a T_m upon first heating. However, no melting transition temperature is observed upon second heating.

Tab. 7. DSC results of the obtained poly(amide urea)s **4a**-**c** and poly(amide urethane urethane)s **6a**-**c**

Sample	Heating / cooling	T_g °C	T_{cr} °C	ΔH_{cr} J·g^{-1}	T_m °C	ΔH_m J·g^{-1}
4a	1. heating	46.5	-	-	197.2	56.6
	cooling	-	169.9	–38.3	-	-
	2. heating	63.1	-	-	-	-
4b	1. heating	57.6	-	-	163.9	47.9
	2. heating	55.5	-	-	-	-
4c	1. heating	49.0	-	-	-	-
	2. heating	72.2	-	-	-	-
6a	1. heating	60.0	-	-	155.9[1]	28.0
	2. heating	35.5	-	-	-	-
6b	1. heating	60.2	-	-		
	2. heating	36.0	-	-	-	-
6c	1. heating	57.1	-	-	160.9	35.5
	cooling	-	111.5	–37.3	-	-
	2. heating	39.0	-	-	159.0[2]	37.0

[1] The sample shows a shoulder at T_m = 161.4°C.

[2] The sample shows a shoulder at T_m = 143.8°C.

Poly(amide urea) **4c** only shows a T_g upon first and second heating. T_m of polymer **4a** is higher than that of **4b**, due to the odd-even effect. Poly(amide urea) **4a** has an

even number, **4b** has an odd number of methylene groups in the diamine unit. T_m of **4a** is close to its decomposition temperature. It is conceivable that T_m of poly(amide urea) **4c** (even number of methylene groups in the diamine unit) is also close to its decomposition temperature and, therefore, cannot be observed.

The obtained poly(amide urethane urethane)s **6a**-**c** upon second heating show lower glass transition temperatures than the poly(amide urea)s **4a**-**c**. The difference between both polymers is merely the repeating units, -NH-CO-O-CH_2-CH_2-O-CO-NH- for the poly(amide urethane urethane)s **6a**-**c** and -NH-CO-NH- for the poly(amide urea)s **4a**-**c**. The *de facto* difference between both repeating units is that the repeating unit of the poly(amide urethane urethane)s has much higher segment mobility because of the high rotational and vibrational freedom of the O-C bonds in comparison with C-C bonds. Furthermore, the hydrogen bond density of the poly-(amide urethane urethane)s is lower than that of the poly(amide urea)s resulting in a lower stiffness of the chains.

Conclusions

Alternating poly(amide urea)s were prepared from ε-caprolactam, diamines, and diphenyl carbonate. The poly(amide urea)s have high melting points despite their relatively low molecular weights. Therefore, these polymers are perfect building blocks for multiblock copolymers. They can be used as hard segments in combination with soft segments to obtain thermoplastic elastomers.

The obtained poly(amide urethane urethane)s derived from ε-caprolactam, diamines, and ethylene carbonate in the second heating show lower glass transition temperatures than the poly(amide urea)s. This phenomenon is in accordance with the common knowledge about polyurethanes and polyureas and is explained by the difference in segment mobility of the repeating units.

[1] Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; "*Encyclopedia of Polymer Science and Engineering*", vol. *11*, 2nd edition, John Wiley and Sons, New York **1988**, p. 315.

[2] Oertel, G.; "*Polyurethane Handbook*", 2nd edition, Hanser Publishers, Munich **1993**.

[3] Allen, G.; Berington, J. C.; "*Comprehensive Polymer Science*", vol. *5*, Pergamon Press, Oxford **1989**, p. 413.

[4] Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; "*Encyclopedia of Polymer Science and Engineering*", vol. *13*, 2nd edition, John Wiley and Sons, New York **1988**, p. 243.

[5] Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; "*Encyclopedia of Polymer Science and Engineering*", vol. 13, 2nd edition, John Wiley and Sons, New York **1988**, p. 212.

[6] Castaldo, L.; De Candia, F.; Maglio, G.; Palumbo, R.; Strazza, G.; *J. Appl. Polym. Sci.* **1982**, *27*, 1809.

[7] Jonas, F.; Meier, H. M.; Pielartzik, H.; Freitag, D.; *Kunstoffe* **1995**, *85*, 1079.

[8] Grigat, E.; Salewski, K.; Timmermann, R.; Koch, R.; *Kunstoffe* **1997**, *87*, 63.

[9] Grigat, E.; Koch, R.; Timmermann, R.; *Polym. Degrad. Stabil.* **1998**, *59*, 223.

[10] Robertz, B.; Keul, H.; Höcker, H.; *Macromol. Chem. Phys.* **1999**, *200*, 1041.

[11] Wiegand, S.; Steffen, M.; Steger, R.; Koch, R.; *J. Environ. Polym. Degrad.* **1999**, *7*, 145.

[12] Mohanty, A. K.; Misra, M.; Hinrichen, G.; *Macromol. Mater. Eng.* **2000**, *276/277*, 1.

[13] Okada, M.; *Prog. Polym. Sci.* **2002**, *27*, 87.

[14] Fey, T.; Keul, H.; Höcker, H.; *Macromol. Chem. Phys.* **2003**, *204*, 591.

[15] Fey, T.; Keul, H.; Höcker, H.; *e-Polymers* **2003**, no. 1.

[16] Fey, T.; Keul, H.; Höcker, H.; *Macromolecules* **2003**, *36*, 3882.

[17] Fey, T.; Hoelscher, M.; Keul, H.; Höcker, H.; *Polym. Int.* **2003**, *52*, 1625.

[18] Mormann, W.; Tiemann, N.; Turuskan, E.; *Polymer* **1989**, *30*, 1127.

[19] Sharma, B.; Ubaghs, L.; Keul, H.; Höcker, H.; Loontjens, T.; van Benthem, R.; in preparation.

[20] Sharma, B.; Ubaghs, L.; Keul, H.; Höcker, H.; Loontjens, T.; van Benthem, R.; in preparation.

[21] Puffr, R.; V. Kub´anek, V.; editors; "*Lactam-based polyamides*", vol. *1*, '*Polymerization, structure, and properties*', CRC Press, Inc., Boca Raton, FL **1991**, pp. 275 ff (and refs. cited therein).